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Synthesis of Monoselenoacetals Using Diisobutylaluminium Benzeneselenolate

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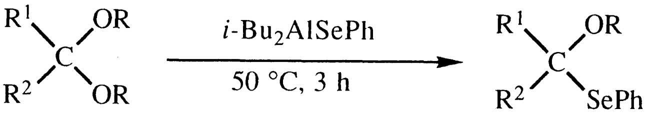
Monoselenoacetals can be synthesized from the reaction of acetals with diisobutylaluminium benzeneselenolate (*i*-Bu$_2$AlSePh) under mild conditions in good yields. Diselenoacetals are also obtained by treating acetals with large excess amount of *i*-Bu$_2$AlSePh.

Monoselenoacetals are synthetically useful reagents,1) and yet only very limited methods have been developed for the synthesis of these compounds.1, 2) In this paper, we wish to report a convenient transformation of acetals into the corresponding monoselenoacetals by the use of diisobutylaluminium benzeneselenolate (*i*-Bu$_2$AlSePh) (Eq. 1).3)



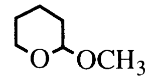
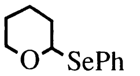
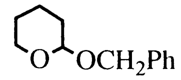
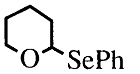
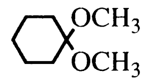
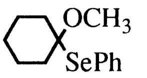
(1)

When dimethoxymethane was treated with *i*-Bu$_2$AlSePh, generated in situ from diphenyl diselenide and a toluene solution of diisobutylaluminium hydride,6) at 40 °C for 5 h, methoxy(phenylseleno)methane was formed in 98% yield (run 1). A similar reaction is applicable to a variety of acetals (Table 1).7) In all cases except for PhCH(OCH$_3$)$_2$, monoselenoacetals have been synthesized in good yields with excellent selectivity. Similarly, Et$_2$AlSeEt serves as a selenolate agent (run 3). Of special interest is that alkyl methoxymethyl ether is converted into the corresponding alkyl phenylselenomethyl ether highly selectivety (run 7). On the other hand, cyclic ethers bearing an α-alkoxyl moiety gave cyclic monoselenoacetals in moderate yields (runs 8 and 9). The acetals of acyclic and cyclic ketones gave less satisfactory results under the same reaction conditions, but good results were obtained by the reaction under the conditions using 2 mol equiv amount of *i*-Bu$_2$AlSePh at 0 °C for 1 h (runs 10 and 11).

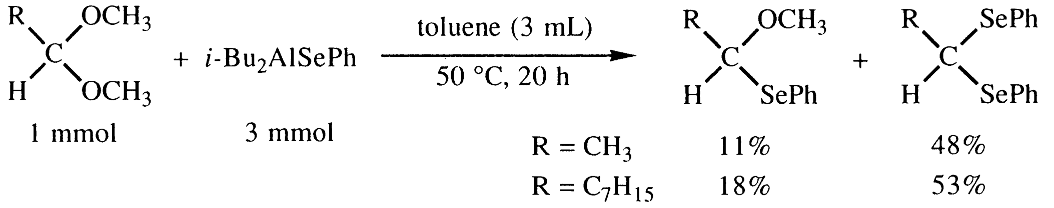
Hoping to find out further utilization of *i*-Bu$_2$AlSePh, we have investigated the synthesis of diselenoacetals by the reaction of i-Bu$_2$AlSePh with acetals. Treatment of the acetals with 3 mol equiv of *i*-Bu$_2$AlSePh at 50 °C for 20 h gave rise to the corresponding diselenoacetals as the major products (Eq. 2).

Further investigations on mechanism of the present reaction and its synthetic application are in progress.

Table 1. Synthesis of Monoselenoacetals

Run	Acetal	Products (%, yield)[a, b]
1[d]	$CH_2(OCH_3)_2$	$CH_2(OCH_3)SePh$ (98)[c]
2	$CH_2(OC_2H_5)_2$	$CH_2(OC_2H_5)SePh$ (87)[c]
3[e]	$CH_2(OC_2H_5)_2$	$CH_2(OC_2H_5)SeC_2H_5$ (84)[c]
4	$CH_3CH(OCH_3)_2$	$CH_3CH(OCH_3)SePh$ (75)
5	$C_7H_{15}CH(OCH_3)_2$	$C_7H_{15}CH(OCH_3)SePh$ (100)[c]
6[f]	$PhCH(OCH_3)_2$	$PhCH(OCH_3)SePh$ (34) $PhCH(SePh)_2$ (28)
7	$C_6H_{13}OCH_2OCH_3$	$C_6H_{13}OCH_2SePh$ (69) $PhSeCH_2OCH_3$ (7)
8		 (58) $HOC_4H_8CH(OCH_3)SePh$ (29)
9		 (53) $HOC_4H_8CH(OCH_2Ph)SePh$ (32)
10[g]	$(CH_3)_2C(OCH_3)_2$	$(CH_3)_2C(OCH_3)SePh$ (86)
11[g]		 (76)

a) Isolated yields. b) Based on acetal. c) GLC yields. d) 40 °C, 5 h. e) $Et_2AlSeEt$ was used instead of i-$Bu_2AlSePh$. f) 30 °C, 5 h. g) i-$Bu_2AlSePh$ (2.0 equiv.), 0 °C, 1 h.



(2)

References

1) D. Seebach, N. Meyer, and A. K. Beck, *Justus Liebigs Ann. Chem.*, **1977**, 846; H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, **101**, 6638 (1979); A. P. Brunetiere and Y. J. Lallemand, Tetrahedron Lett., **29**, 2179 (1988).

2) D. L. J. Clive and S. M. Menchen, *J. Org. Chem.*, **44**, 1883 (1979); I. I. Lapkin, N. N. Pavlova, A. N. Nedugov, and G. A. Gartman, *Zh. Org. Khim.*, **16**, 1623 (1980).

3) The reaction of acetals with i-Bu_2AlSPh[4] and i-$Bu_2AlTePh$[5] has been reported.

4) Y. Masaki, Y. Serizawa, and K. Kaji, *Chem. Lett.*, **1985**, 1933.

5) K. Sasaki, T. Mori, Y. Doi, A. Kawachi, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1991**, 415.

6) K. Maruoka, T. Miyazaki, M. Ando, Y. Matsumura, S. Sakane, K. Hattori, and H. Yamamoto, *J. Am. Chem. Soc.*, **105**, 2831 (1983).

7) All new compounds in this paper were characterized by elemental and spectroscopic analysis.

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